

SYNTHESIS OF ALCOHOLS FROM SYNGAS AND ALCOHOL CHAIN GROWTH OVER COPPER-COBALT BASED CATALYSTS

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ABSTRACT: The alcohols synthesis were studied over copper-cobalt catalysts from syngas under pressure (6.0 MPa). The higher alcohols formation was enhanced with the cobalt content, caused probably by an increase of the number of Co-Cu bisites, and the higher hydrocarbons augmented simultaneously, explained by common reactional intermediates. The cobalt quantity on the surface influences the chain growth evolving into alcohols or hydrocarbons. It was shown that an augmentation of CO insertion and a modification of the hydrogenation property of system could be responsible of these effects, as supported by the tests of reactivities and those of probe molecules. It was illustrated that some strong interactions existed between cobalt and copper, and the influences of different pretreatments were also investigated.

1. INTRODUCTION

The syngas conversion remains one of the most interesting reactions in heterogeneous catalysis. Especially since the two energy crisis in the world, the more effective utilisations of syngas have attracted much attention [1,2]. With different catalysts and operational conditions, it could be oriented into methanolation, methanation, olefin production via Fischer-Tropsch reactions, synthesis of ethanol or acetyl aldehyde over Rhodium catalysts, or synthesis of mixed alcohols, etc. In that mixed alcohols production, the main problems were carbon chain growth, high alcohol activity and good selectivity. Several catalytic systems have been proposed [2], the copper-cobalt catalysts seem to be the most promising [1-3].

In this work, the influences of cobalt additives onto copper based catalysts were investigated, as well as the effects of pretreatments and those of supports, the temperature programmed reduction (TPR) and CO chemisorption were performed for the catalyst characterizations, the results of probe molecule tests were also discussed.

2. EXPERIMENTAL

2.1. Catalyst preparation: the supports were prepared by the coprecipitation method[4], referred as CuLaZr(i). The catalysts were prepared by impregnating the support with an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to a desired content. The impregnates were dried at 70°C in a flux of argon, and calcined at 350°C in a flux of argon or in air for 5h. They are referred as x%Co/CuLaZr(i).

2.2. Syngas reactions: hydrogenation of CO was carried out in a continuous flow reactor consisting of a 6 mm ID stainless steel tube containing 0.5 g of catalyst under the reaction conditions: $P = 6.0 \text{ MPa}$, $T = 250\text{-}280^\circ\text{C}$, $\text{H}_2/\text{CO} = 2$, $D = 4 \text{ l/h/g}$. The reaction products were analysed by gas chromatography.

2.3. Probe molecule tests: the samples (0.5g) were reduced in hydrogen over night, then brought into contact with synthesis gas ($P = 0.1 \text{ MPa}$, $T = 225^\circ\text{C}$). After reaching a stationary state, a small amount (2 mol%) of probe molecules (C_2H_4) were sent into the CO/H_2 stream and the generated gases were analysed by gas chromatography with flame ionization detector [5,6].

3. RESULTS AND DISCUSSION

3.1. Influence of cobalt additive

The alcohols synthesis were studied over cobalt modified copper catalysts, six samples with different cobalt content were prepared and investigated. For the monometallic copper sample CuLaZr(1), it has almost no chain growth, the higher alcohol fraction was only 0.2%. With the cobalt addition, the higher alcohols (C_2+OH) formation was enhanced, and it increases with the rise of cobalt content, as does the yield into higher hydrocarbons (C_2+HC) and that of total hydrocarbons. The simultaneous augmentation of C_2+OH and C_2+HC (Fig.1a) was explained as that there were common intermediates for their formation [7,8].

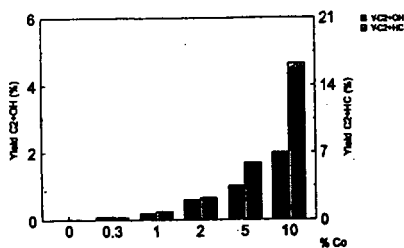


Fig. 1a. Yields in C_2+OH and in C_2+HC
— Influence of cobalt content

As suggested, during the growth of hydrocarbonated chain, there is a competition between the CH_2^* addition (formed on cobalt) which leads to the hydrocarbons formation, and the insertion of oxygenated species (formyl or CO, formed on copper) which results in alcohols. Thus the cobalt quantity on the surface influences the chain growth evolving into the alcohols or the hydrocarbons.

In the case of the production into higher alcohols C_2+OH and their fraction in total alcohols, both increase with the rise of the cobalt content (Fig. 1b).

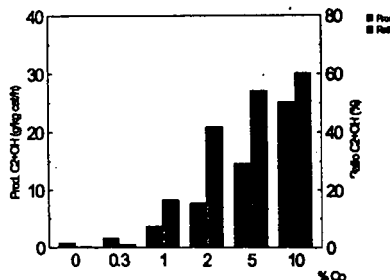


Fig. 1b. Higher alcohols productivity and ratio in total alcohols
— Influence of cobalt content

3.2. Effect of pretreatment

A pretreatment of the precursor after impregnation may be favorable to the decomposition of $Co(NO_3)_2$ and the formation of Co_3O_4 , which results in a modification of the reducibility of the catalyst and eventually the formation of mixed oxides. We have compared the pretreatments operating at the temperatures between 350°C and 700°C, in an inert flux (argon) or in air environment (21% O_2).

As illustrated in Fig.2, the catalytic activity decreases while the calcination temperature rises, and the best results of the alcohol production and the higher alcohol ratio (C_2+OH/ROH) have been obtained by calcinating at 350°C. When calcinated in air rather than in argon, the catalytic system orient the reactions much more selectively to the alcohols, and the alcohols productivity is also better for the previous system (calcinated in air). So the pretreatment at 350°C in air has been used for the continuation of the work.

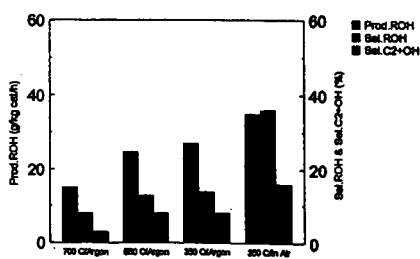


Fig.2. Effect of pretreatment on activities of the catalysts

3.3. Influence of support

In our previous work, several copper based catalysts were investigated. It is the sample CuLaZr(2) which is the most favorable for the methanololation, and it was then utilised as a support in the place of CuLaZr(1) for the preparation of the bimetallic catalyst. In fact, the catalyst 5%Co/CuLaZr(2) gives better results.

The effects of reaction temperature were also studied. It was shown that both yields of alcohols and of hydrocarbons increased with the reaction temperature, and that the selectivity to alcohols pass a maximum of 38.4% at 270°C (Fig.3), and the alcohols productivity was 35.8 g/kg cat/h with higher alcohols ratio of 51.6%.

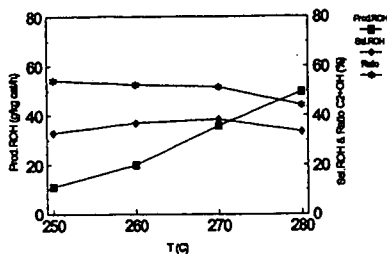


Fig.3. Influence of reaction temperature

3.4. CO chemisorption and TPR

The chemisorption of reactants like CO or H₂ was the slow step in CO/H₂ reactions. The quantity and the form of CO adsorbed are often in relation to the rate and the orientation of the reaction. And the study on CO chemisorption may also give some information of the accessible metallic area after the reduction[9].

The tests of CO chemisorption were made on three types of catalysts (CuLaZr, Co/LaZr, Co/CuLaZr) and the quantities of CO chemisorbed at ambient temperature are compared. It is shown that the addition of cobalt onto CuLaZr decreases the accessible metallic area of the catalyst, as explained by a covering of copper sites by cobalt oxide (more difficultly reducible) on the surface of the catalyst.

The temperature programmed reduction (TPR) tests were performed to see the influence of cobalt additive on the catalyst reducibilities, and the TPR spectra of the above three catalysts were compared. The maximum of the reduction peak of cobalt catalysts were at 316°C and that of copper system was at 218°C. And for the bimetallic system (Co/CuLaZr), there was only a reduction peak with a maximum at 255°C. This phenomenon suggested that there was an interaction between cobalt and copper, which resulted in a simultaneous reduction and a decrease of the Co₃O₄ reduction temperature. This interaction was also reported by Mouaddib [10].

3.5. Probe molecule tests

The effect of ethylene addition is illustrated in Fig.4. It is shown that C₂H₄ addition leads to a great augmentation of propanol, with a diminution of methanol. Propanal (propionic aldehyde) increases simultaneously. This result suggested that there is an insertion of the methanol precursor (like formyl species or CO) to the chemisorbed olefins. The other formed products (like CH₄, C₃H₆₋₈ and C₄H₈₋₁₀, not represented in the figure) change only a little.

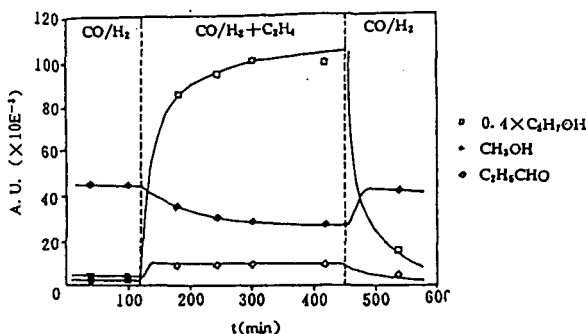


Fig. 4. Effect of C_2H_4 addition to syngas stream as a probe molecule

As discussed by Chuang et al.[5], the insertion of C_1 oxygenated species (CO or formyl) into hydrocarbonated entities has particular importances as an indication of the growth of the oxygenated products. The comparison with the results of monometallic system is represented in Fig. 5. It is observed that only over bimetallic catalyst a great augmentation of the C_3H_7OH formation has been achieved. It means that the simultaneous presence of copper and cobalt is important for a good chain growth formation into the alcohols.

The ratios $C_2H_6/(C_2H_4+C_2H_6)$ and C_3H_7OH/C_2H_5CHO may be good indications for the hydrogenating properties of the systems. It is observed that ethane represents 99.7% of total C_2 hydrocarbon over the catalyst CuLaZr, which indicates a great hydrogenating property of the system. However, the chain growth on this system is very low. For the catalyst Co/LaZr, the ratio of $C_2H_6/(C_2H_4+C_2H_6)$ is 2.1%, which indicates a weak hydrogenating property of the system, which may be in relation to its weak activity. In the case of Co/CuLaZr, the ratio of $C_2H_6/(C_2H_4+C_2H_6)$ is 20.5%, and C_3H_7OH/C_2H_5CHO is 30, which indicated a good hydrogenating property of the system.

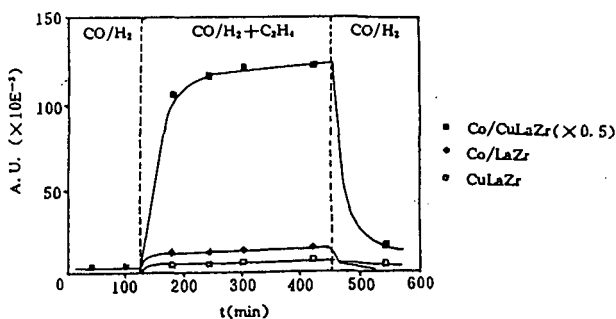


Fig. 5. Effect of C_2H_4 addition to syngas on C_3H_7OH formation

4. CONCLUSION

It was shown that there were some strong interactions between cobalt and copper, and their simultaneous presence was important for a good orientation for the alcohol formation. And the addition of cobalt onto CuLaZr system may have three important effects on the higher alcohol production: an increase of the formation of hydrocarbonated species, an augmentation of the CO insertion property of the system, and a modification of the hydrogenating property of the catalyst, as supported by the tests of reactivities and those of probe molecules. With different pretreatment, the results show that the calcination at $350^\circ C$ in air was most favorable.

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